INTERACTIVE EFFECTS IN NITROGEN COMPOUND INDUCED STORAGE INSTABILITY IN SHALE DERIVED DIESEL FUEL

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INTRODUCTION

The autoxidation of middle distillate fuels during periods of storage has been a continuing problem in the utilization of these liquids by the government and commercially. With diesel fuels, instability is commonly defined by the formation of sediments, gums, color bodies and by the accumulation of hydroperoxides. Gravimetric accelerated storage stability tests conducted with model compounds as dopants in otherwise stable distillate fuels have demonstrated that oxidative condensation reactions of polar heterocycles are often deleterious to stability (2-15). In particular, nitrogen containing aromatics (pyrroles, pyridines, indoles, etc.) appear to be very harmful. Correlation of model dopant studies with results obtained with actual unstable fuels has indicated that the autoxidation processes are usually not isolated reactions but are sensitive to the presence of other fuel constituents (11, 13). Certain oxygen and sulfur compounds have been found to markedly alter the extent of model nitrogen compound induced storage instability in both middle distillate and model fuels (3, 4, 6, 16-18). Little is known about the chemical mechanisms of such interactive effects in fuel instability, and possible explanations include acid/base catalysis of oxidation and condensation pathways as well as involvement in radical chain processes. Interactions between different types of nitrogen compounds have also been studied to a limited extent (6, 10), and may similarly be of great importance in actual complex fuels.

As part of an effort to learn more about potential interactive effects, we have examined the autoxidation of two model nitrogen compounds, 2,5-dimethylpyrrole (DMP) and 3-methylindole (3-MI), in a shale diesel fuel in the presence of a second model dopant (t-butylhydroperoxide, an organic acid, or an organic base). The decision to examine DMP and 3-MI as nitrogen compound dopants was based upon a body of earlier work which analyzed the autoxidation behavior of these compounds (in the absence of other externally added active species) in the identical shale base fuel and under identical storage stability test conditions (10-12, 14, 15).

EXPERIMENTAL

Storage Test Techniques

The accelerated storage stability test method used has been described in detail (10-12). Hydroperoxide values were determined in stressed fuel samples following filtration through glass fiber filter paper by iodometric titration (ASTM D-1583-60).

Instrumental Methods

Infrared spectra were obtained as KBr pellets on a Perkin-Elmer Model 681 instrument with a Model 3600 data station (PECDS software). Solution proton nmr spectra were obtained in d_5-pyridine or deuterated chloroform with a Varian EM-390 90 MHz instrument. Elemental analyses were accomplished with a Carlo Erba Model 1106 elemental analyzer. Routine GC separations were made on either a Varian Model 3700 or a Perkin-Elmer Model 3920B gas chromatograph equipped with fused silica capillary columns (OV-101, 50 m x 0.3 mm) and FID detection.

Reagents

The base fuel for the present study was diesel fuel refined from Paraho crude shale oil by SOHIO. This fuel was produced in the U.S. Navy's Shale-II demonstration and is well-characterized (10). A quantity of this fuel was available which contained 24 mg/l of 2,4-dimethyl-6-t-butylphenol (AO-30) as the only additive (designated at NRL as fuel sample "D-11"). The D-11 fuel contained 15 ppm N (w/v) and exhibited good storage stability (10). All compounds used as dopants were pure by nmr, capillary GC, and/or mp. Fresh DMP was stored frozen under a nitrogen atmosphere to prevent autoxidation and it remained colorless under this storage. The concentration matrices for the interactive experiments were prepared so that effects of concentration (of both the DMP or 3-MI and the co-dopant) and of venting of test flasks could be assessed. In instances where the co-dopant was appreciably soluble in the D-11, two concentration levels were used (9.64×10^{-3}M and 3.21×10^{-2}M), which correspond to equivalent nitrogen compound (DMP or 3-MI) concentration levels of 135 and 450 ppm N (w/v). The construction of a 2 x 2 test matrix with both dopants then involved duplicate test flasks at each possible pairing, with additional flasks providing baseline "blank" values for D-11 doped with just the nitrogen compound, just the co-dopant, and the undoped D-11 fuel. In cases where the co-dopant exhibited only limited solubility in the D-11 fuel, a saturated solution was employed.

RESULTS AND DISCUSSION

Autoxidation of DMP and 3-MI in the Presence of t-Butylhydroperoxide (TBHP)

Previous storage stability tests employing DMP and 3-MI as dopants in a stable shale diesel fuel base indicated that while both compounds deteriorated the quality of the fuel, the nature of their instability processes differed substantially (11, 14). The results obtained with DMP and 3-MI are compared below:

Table 1
Comparison of DMP and 3-MI Induced Storage Instability

Property	3-MI	DMP
Induction Period:	yes	not observed
Peroxide Level After Stress (Relative to Fuels Blanks):	slightly less (80°C)	much less (80°C)
	slightly more (43°C)	much less (43°C)
Effect of Venting:	large	minimal
Effect of AO-30:	large	minimal
Reaction Order in Dopant:	?	1.0
Formula of Dopant:	C_9H_9N	C_6H_9N
Empirical Formula of Sediment:	$C_{15.8}H_{15.2}NO_{2.6}$	$C_{6.3}H_{6.7}NO_{1.6}$

Since the storage stability characteristics of these dopants had been examined in detail, it was considered of interest to compare both of these compounds in the context of interactive experiments. The initial study involved the addition of a model nitrogen compound to fuel D-11 together with a hydroperoxide as co-dopant. The hydroperoxide selected was t-butylhydroperoxide since it is available commercially in high purity. The goal of the experiments was to survey the importance of the accumulation of hydroperoxides in a complex fuel in influencing the formation of insolubles during stress when a particular class of nitrogen heterocycles is present.

Accelerated storage stability tests employing DMP and TBHP as co-dopants in fuel D-11 were run at both 80°C (7 and 14 days) and 43°C (49 and 92 days). The gravimetric results, summarized in Table 2, indicated that a definite positive (synergistic) interaction existed between the DMP and TBHP under all conditions examined. The concentration matrix which was studied used DMP at two levels: Lo DMP

= 135 ppm N w/v, equivalent to 9.64×10^{-3} M; and Hi DMP = 450 ppm N (3.21×10^{-2}M). The levels of TBHP used corresponded to the same molar concentration values. Thus, the relative concentration matrix which was used was therefore (expressed as moles of TBHP added/moles of DMP added): Lo TBHP/Lo DMP = 1.0, Lo TBHP/Hi DMP = 0.3, Hi TBHP/Lo DMP = 3.3, Hi TBHP/Hi DMP = 1.0. The results of hydroperoxide analyses also appear in Table 2, and are given as peroxide numbers (ASTM D-1583-60).

Table 2
Storage Stability Test Results for the DMP/TBHP Interaction

| Sample* | Total Insolubles, mg/100 ml (Peroxide Number, meq ROOH/kg fuel) | | | |
	80°C/7d	80°C/14d	43°C/49d	43°C/92d
Fuel Blanks	0.5(0.9)	0.0(3.0)	0.0(0.3)	0.0(1.0)
Lo TBHP Blanks	0.4(39.5)	0.9(34.2)	0.0(58.9)	0.0(17.2)
Hi TBHP Blanks	0.5(80.8)	0.7(84.6)	0.0(100.5)	0.0(60.9)
Lo DMP Blanks	30.2(0.2)	47.4(0.4)	25.4(0.0)	42.6(0.0)
Hi DMP Blanks	89.6(0.0)	171.4(0.2)	97.3(0.0)	153.7(0.0)
Lo TBHP/Lo DMP	37.9(18.8)	80.0(47.1)	33.2(70.6)	59.1(12.6)
Lo TBHP/Lo DMP/v	37.0(16.0)	81.3(70.4)	32.2(63.2)	60.5(10.2)
Lo TBHP/Hi DMP	101.3(7.5)	183.9(12.4)	113.8(22.4)	200.6(5.8)
Lo TBHP/Hi DMP/v	101.3(6.0)	193.9(7.3)	134.5(0.8)	215.2(4.2)
Hi TBHP/Lo DMP	62.7(63.3)	92.0(80.8)	79.4(33.4)	93.7(61.2)
Hi TBHP/Lo DMP/v	66.1(64.0)	95.7(93.8)	72.8(39.2)	95.5(116.5)
Hi TBHP/Hi DMP	160.4(25.0)	257.0(28.0)	233.2(57.3)	277.8(11.2)
Hi TBHP/Hi DMP/v	171.8(15.2)	267.5(20.7)	249.9(106.0)	325.3(47.8)

*The vented test flask trials are those denoted by "v".

In all instances, the presence of TBHP significantly increased the yield of insolubles produced when DMP was also present. Furthermore, the presence of Hi TBHP levels was always associated with more sediment than the corresponding Lo TBHP trials. In examining the peroxide number data, it will be noted that the correlation between the ultimate hydroperoxide levels and the yields of sediment are not good, which is an expected result (10, 11). The peroxide number of unstressed, doped D-11 fuel containing Lo TBHP was 20.7, and 68.9 for Hi TBHP. When DMP was not present, the TBHP dopant did not exert a significant destabilizing effect upon the fuel as measured by sediment generation. The effects of venting of test flasks were seen to be small and variable. Curiously, high levels of hydroperoxide were often observed in some Hi DMP trials after stress when TBHP had been present. Earlier work from our laboratory had indicated that DMP, in the absence of externally added hydroperoxide, was associated with very low peroxide numbers after stress.

A similar experimental matrix was used in the study of the potential interaction between 3-MI and TBHP. Interest in examining this interaction originated with our earlier studies of 3-MI induced fuel instability (11, 14), which showed that 3-MI is able to promote the formation of sediment and gum, but only in the absence of a hindered phenol antioxidant (AO-30). This result, coupled with the existence of a long induction period in the autoxidation of 3-MI in our shale diesel fuels, suggested that a classical free radical mechanism may be involved, which should, in turn, be sensitive to the presence of hydroperoxide present in the fuels.

Storage stability test results for the 3-MI/TBHP interaction are given in Table 3. These results indicate that a synergistic effect is present. Comparison of the 7 and 14 day results at 80°C suggest that an induction period was present. It will be noted that in the absence of externally added TBHP, 3-MI does not effectively promote sediment formation in the D-11 fuel, which contains AO-30. There is little doubt that the addition of TBHP rapidly overwhelmed the antioxidant, present at a level which was somewhat less than 24 mg/l, thereby allowing the autoxidation of 3-MI to proceed. The highest amounts of total insolubles were formed in the 43°C tests.

Venting of the test flasks generally led to a marked increase in the amount of sediment which formed. In these respects, the TBHP induced oxidation of 3-MI in fuel D-11 appears to be very similar to the simple autoxidation of this model nitrogen compound in fuel D-1 (a fuel which is identical in all respects to fuel D-11 except that it does not contain antioxidant) (11). Table 3 also shows peroxide analysis data for one of the stress sets (43°C/91d), which clearly indicates that high levels of hydroperoxide were present in all of the experimental flasks.

Table 3
Storage Stability Test Results for the 3-MI/TBHP Interaction

| Sample* | Total Insolubles, mg/100 ml (Peroxide Number, meq ROOH/kg fuel) | | | |
	80°C/7d	80°C/14d	43°C/49d	43°C/91d
Fuel Blanks	0.0	0.1	0.2	0.0(0.8)
Lo TBHP Blanks	0.0	0.4	0.0	0.0(16.2)
Hi TBHP Blanks	0.6	0.7	0.0	0.0(60.5)
Hi 3-MI Blanks	0.2	0.8	---	---
Lo TBHP/Lo 3-MI	0.7	1.1	0.3	0.0(50.2)
Lo TBHP/Lo 3-MI/v	0.4	3.9	0.5	0.0(76.6)
Lo TBHP/Hi 3-MI	1.5	11.7	2.2	53.6(46.3)
Lo TBHP/Hi 3-MI/v	2.3	12.5	70.7	129.0(36.6)
Hi TBHP/Lo 3-MI	0.7	3.8	2.5	3.7(112.5)
Hi TBHP/Lo 3-MI/v	0.6	4.1	1.5	9.3(159.9)
Hi TBHP/Hi 3-MI	1.7	8.7	33.0	0.7(64.2)
Hi TBHP/Hi 3-MI/v	1.9	17.2	81.2	149.5(56.3)

*The vented test flask trials are those denoted by "v".

Analyses of the sediments obtained with both DMP and 3-MI in the course of these TBHP interactive experiments have indicated that they are very similar, both in elemental composition and spectroscopic character, to sediments obtained in the absence of TBHP. For DMP, a typical sediment obtained in the presence of TBHP is 10.7% N, 60.1% C and 5.5% H; for 3-MI, a typical analysis is 5.5% N, 71.3% C and 5.6% H (these compare favorably with the empirical formulas in Table 1). Thus, it would appear that the TBHP functions as a catalyst or radical initiator rather than as a reactant in sediment formation.

Autoxidation of DMP and 3-MI in the Presence of Organic Acids and Bases

In an extension of our study of interactive effects in the autoxidation of DMP and 3-MI, ten organic acids and bases were examined as co-dopants in fuel D-11. This work was intended to determine whether the autoxidation of the nitrogen compounds is subject to acid or base catalysis, or if condensation products could form in lieu of true catalysis. Ten co-dopants were selected for study: acetic acid (HOAc), hexanoic acid (HA), decanoic acid (DA), p-toluenesulfonic acid (p-TsOH), dodecylbenzene sulfonic acid (DBSA), nicotinic acid (NA), 3-pyridinesulfonic acid (3-PSA), tri-n-butylamine (TBA), N,N-dimethylaniline (DMA) and 4-dimethylaminopyridine (4-DMAP). Most of the co-dopants were examined at two concentration levels ("Hi" and "Lo", as with TBHP); however, some of the compounds were only slightly soluble in D-11, so that a saturated solution was used for these (p-TsOH, NA, 3-PSA). Accelerated storage stability was assessed at 80°C (14d).

With DMP, the carboxylic acids (HOAc, HA and DA) all interacted in a synergistic fashion to increase the amount of sediment generated. A typical set of data is given in Table 4 for the DMP/DA experimental set. The results with the sulfonic acids were more difficult to interpret. Thus, DBSA exhibited a very strong positive interaction with DMP when present at levels of 0.3 or 1.0 equivalent. Yet when all four test flasks (vented and unvented) of the Hi DBSA/Lo DMP interaction were examined (these contain 3.33 equiv. of DBSA relative to DMP) a strong negative

interactive effect was seen. The interactive effects for p-TsOH were seen to be small in magnitude and variable. A very potent base catalyst, 4-DMAP, was observed to interact with DMP in a positive fashion whenever it was present. By contrast, interaction with other base catalysts (TBA, DMA) or low-solubility zwitterionic species (NA, present at ca. 0.3 ppm N w/v, and 3-PSA, present at less than 0.2 ppm N w/v) did not lead to significant synergism under these test conditions.

Table 4
Storage Stability Test Results for the DMP/DA Interaction
Fuel D-11 - 80°C/14 days - mg/100 ml

Sample*	Filtered Sediment	Adherent Gum	Total Insolubles
Fuel Blanks	0.1	0.0	0.1
Lo DA Blanks	0.1	0.1	0.2
Hi DA Blanks	0.1	0.1	0.2
Lo DMP Blanks	45.0	2.4	47.4
Hi DMP Blanks	165.2	6.2	171.4
Lo DA/Lo DMP	82.7	3.0	85.7
Lo DA/Lo DMP/v	84.2	2.6	86.8
Lo DA/Hi DMP	247.7	5.8	253.5
Lo DA/Hi DMP/v	238.8	5.3	244.1
Hi DA/Lo DMP	78.4	2.3	80.7
Hi DA/Lo DMP/v	96.2	2.6	98.8
Hi DA/Hi DMP	264.0	5.0	269.0
Hi DA/Hi DMP/v	279.2	5.3	284.5

*The vented test flask trials are denoted by "v".

Elemental and spectroscopic analyses were applied to the samples of DMP induced sediment from these interactive experiments. It was not possible to obtain an elemental analysis from the sediment formed in the DMP/DBSA trials, as their tarry/waxy nature precluded proper sampling technique. However, the incorporation of molecules of DBSA into the sediment is implied by: (a) the fact that such a large amount of sediment (up to 1300 mg/100 ml) was generated that the DMP alone is unable to account for the mass, and (b) a number of complex absorption peaks appear in the S=O/S-O region of the infrared. Thus, the DBSA may serve as a reactant in addition to or instead of serving as a catalyst. The incorporation of sulfur into DMP-derived sediments has been observed by other workers when thiophenol was used as a co-dopant (16-18); it has been considered possible that in situ oxidation of thiols to sulfonic acids may be a viable pathway (4, 6). The DMP-derived sediments produced in all nine other interactive experiments proved to be remarkably similar to the insoluble material generated by DMP without co-dopant. Thus, it would appear that the carboxylic acids and 4-DMAP are serving as true catalysts.

In a similar manner, the interaction of 3-MI with the ten acid/base co-dopants was examined in D-11 fuel using 80°C-14d storage stability tests. With the three carboxylic acids (HOAc, HA and DA), synergism was noted, with the highest levels of insoluble material present in Hi 3-MI flasks (ca. 6-60 mg/100 ml of sediment was generated, as compared with 0.8 mg/100 ml in the flasks which contained only 3-MI). Venting of test flasks seemed to be associated with higher levels of sediment. As was the case for DMP, the interactive effects of 3-MI with the sulfonic acids were difficult to interpret. With p-TsOH, the interactive effect was uniformly small and indeterminant. With DBSA, it was possible to generate small quantities of sediment under most conditions, but only one set of conditions (Hi DBSA/Hi 3-MI/unvented) led to the formation of large amounts of solids (ca. 70 mg/100 ml). With 4-DMAP, base catalysis of 3-MI autoxidation was not evident. In light of the superior catalytic nature of 4-DMAP, this result was somewhat unexpected, especially in light of a recent suggestion that base-catalyzed oxidation of 3-MI could be significant (19). Nicotinic acid (NA) was found to be catalytic in its interaction with 3-MI, with a maximum of ca. 30 mg/100 ml of sediment formed in the Hi 3-MI/vented trials (a

saturated solution of NA was used, 0.3 ppm N w/v). Despite the apparent failure of 4-DMAP, dimethylaniline (DMA) exhibited synergism with 3-MI, but the effect was largest when DMA was present at a "Lo" level. Tri-n-butylamine (TBA) actually appeared to inhibit the autoxidation of 3-MI slightly. The final co-dopant, 3-pyridinesulfonic acid (3-PSA) showed a very slight positive interactive effect, forming ca. 6 mg/100 ml of solids in the Hi 3-MI flasks.

Analysis of the sediments generated in the 3-MI interaction experiments was limited by the small amounts of materials isolated on the glass fiber filter pads. Elemental analyses could only be conducted on the sediments from the carboxylic acid interactions; these all contained ca. 5.7% N, 72.5% C and 5.8% H, and so are almost identical in elemental composition to 3-MI induced sediment which formed in the absence of the co-dopants. Spectroscopic examination of the sediments confirm that the heterogeneous material generated is also similar. Table 5 is a qualitative summary of the results obtained with DMP and 3-MI where an organic acid or base was present as a co-dopant.

Table 5
Summary of Relative Interactive Effects with Organic Acids and Bases

Co-Dopant**	Interactive Effect*	
	DMP as Dopant	3-MI as Dopant
HOAc	++	++v
HA	++	++v
DA	++	++
p-TsOH	i	i
DBSA	++	++v
NA	i	++v
3-PSA	i	+
TBA	+v	-
DMA	i	+
4-DMAP	+	i

*Key to symbols: ++ = strong synergism, + = weak synergism
- = weak inhibition, i = indeterminate effect
v = sensitive to venting of test flasks
**Refer to the text for the identity of the abbreviations.

CONCLUSIONS

Hydroperoxide dissolved in a shale derived diesel fuel can interact in a strong synergistic fashion with polar nitrogen heterocyles to lead to the formation of significant amounts of sediment and gum. Carboxylic and sulfonic acids similarly assist in the degradation of fuel quality by interacting with alkylpyrroles and indoles. Interactions with organic bases appear to be of a smaller magnitude.

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